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14. ABSTRACT
Pyrotechnic signals typically generate colored light via photonic emission from thermally-excited states of gas-phase metal combustion products. Blue light can be generated in pyrotechnic compositions with the use of copper-containing compounds as a fuel within the formulation. In the presence of chlorine containing compounds within the composition, these pyrotechnics exhibit emission bands in the blue region of the visible spectrum with peaks observed from 435-480 nm. Color degradation occurs at temperatures above 1200 °C, leading to the hypothesis that the blue emission must arise from a relatively unstable molecular species. Several have hypothesized that this species is likely copper(I) chloride (CuCl) or even the trimeric Cu_3Cl_3, though the identity of this emissive species as either CuCl or Cu_3Cl_3 has been theoretically disputed in the literature with NASA CEA thermodynamic calculations suggesting that excellent blue colors can be achieved with temperatures in excess of 2200 °C. While many of these potential emissive copper-containing species have been empirically characterized, the identity and electronic structure of these copper(I) halide emitters have yet to be fully characterized. Here, we investigate these cuprous halide emitters with the use of flame ionization spectroscopy to measure high-resolution molecular emission spectra of various cupric salts that can be utilized in pyrotechnic signaling devices. These spectroscopically measured visible emission bands will be compared with calculated electronic transitions of candidate emitter species using time-dependent density functional theory to confirm the molecular and electronic identity of the emitters. These techniques will establish methods for the characterization and development of light emitters for next generation visible-light generating pyrotechnic formulations.

15. SUBJECT TERMS
pyrotechnics, copper halides, blue visible light, density functional theory

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Investigation into Blue Light Emission for Copper-containing Pyrotechnics

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Captain J. T. Elder
Commanding Officer
NSWC Crane

Investigation into Blue Light Emission for Copper-Containing Pyrotechnics

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Prepared for: EuroPyro

May, 2015, Toulouse, France

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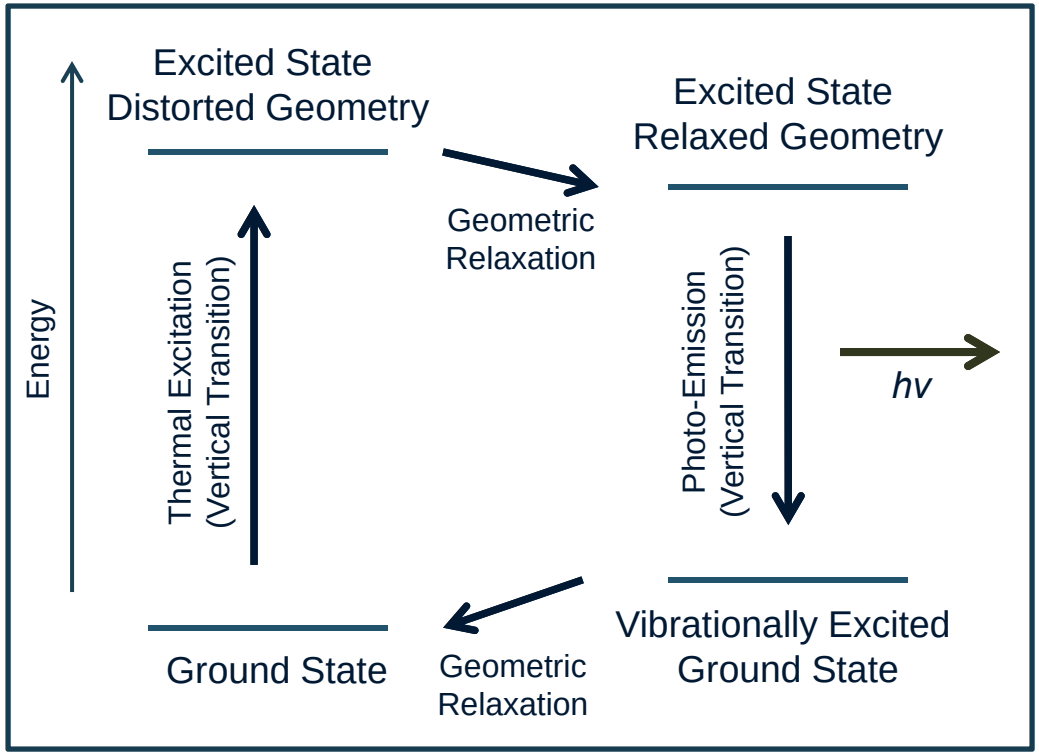
Blue Pyrotechnic Emitters: Background

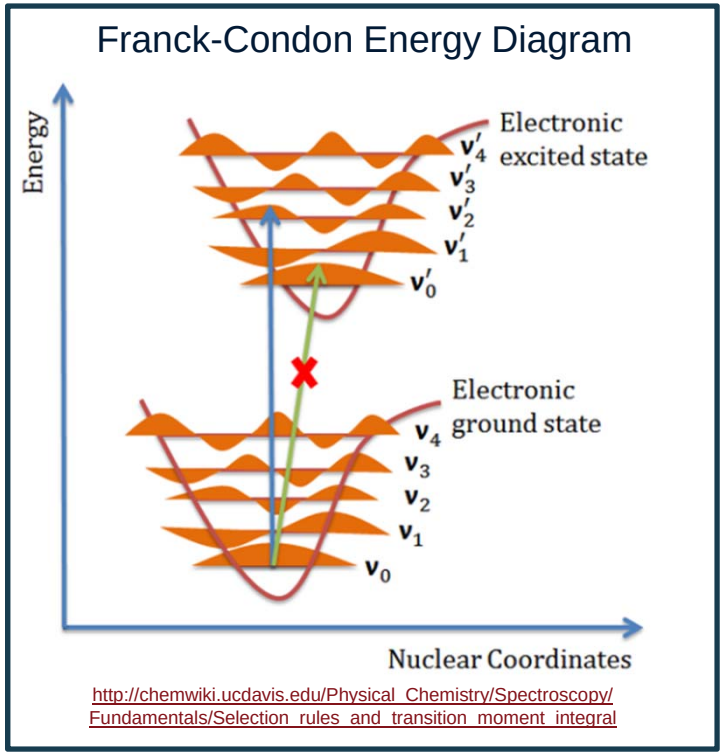
- Blue Pyrotechnic Emitters:
  - Copper Chloride
    - Traditionally identified as CuCl monomer
    - Some dispute[1]: clusters detected via mass spec
    - Clusters know to be photoluminescent[2]
  - Copper Iodide
    - More intense than CuCl[3]
    - No clear explanation as to why

1) Dolata, Propellants, Explosives, Pyrotechnics, *30* (2005), No 1, p 63.
2) Ford, Chemical Reviews, *99*, (1999), pp 3625-3647.
3) Klapötke, Antewandte Chemie, *53*, (2014), 9665 –9668.

Computational Approach for Molecular Emission Analysis

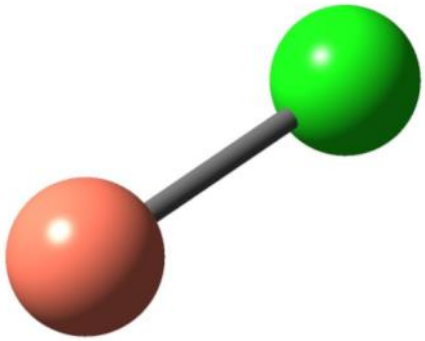
- Quantum mechanics can elucidate differences in molecular emission
- Computational tool: Time-Resolved Density Functional Theory (TD-DFT)
  - Gaussian 09W, B3LYP, Def2-TZPPD[1]
- Calculations will focus on electronic transitions
  - Influence of molecular vibrations—Franck-Condon factors



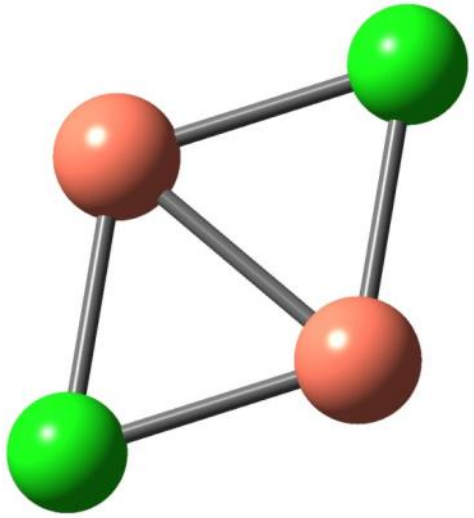


[1]Dmitrij Rappoport and F. Furche, *Property-optimized Gaussian basis sets for molecular response calculations*, **J. Chem. Phys.** 133, 134105 (**2010**).

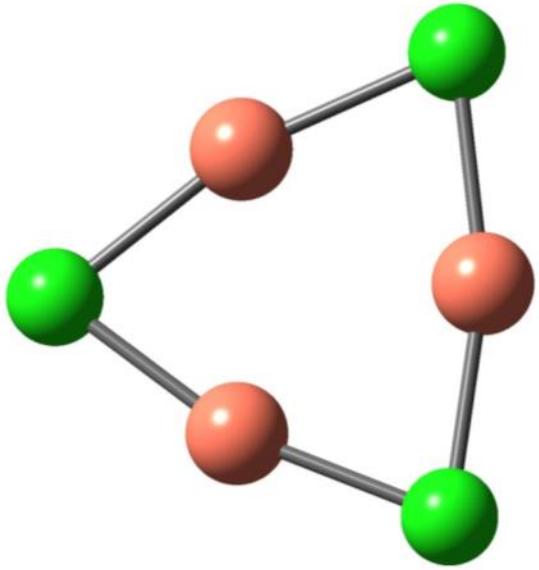
Computational Results: $(CuCl)_n$ Geometries



CuCl Calculated Geometry	
Cu-Cl	2.091 Å

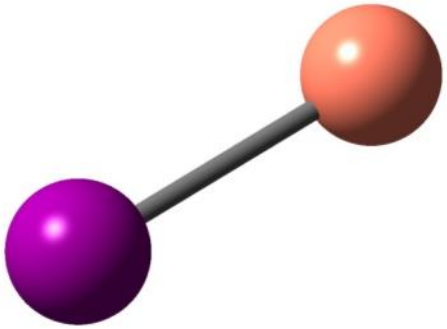


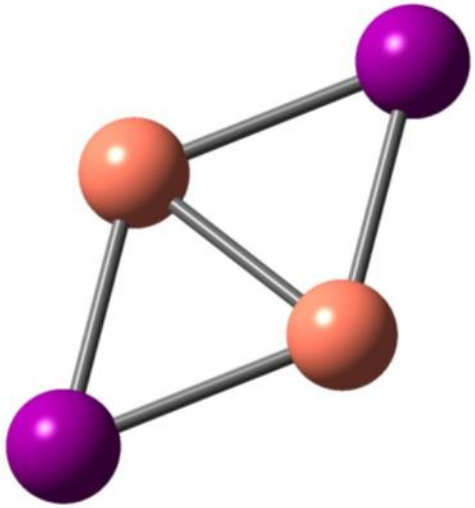
$(CuCl)_2$ Calculated Geometry	
Cu-Cl	2.281 Å
Cu-Cu	2.441 Å
Cu-Cl-Cu	64.7°
Cl-Cu-Cl	115.3°

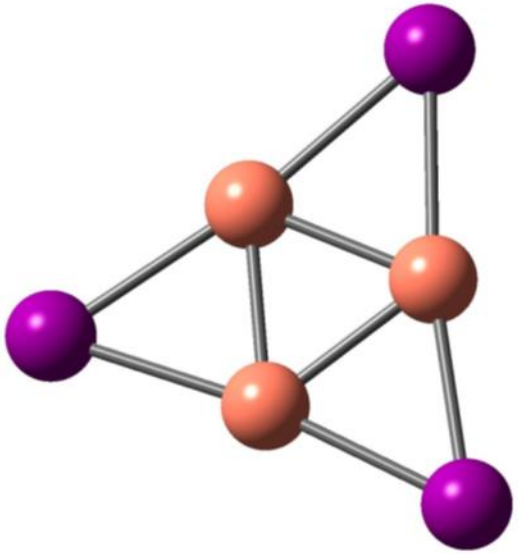


$(CuCl)_3$ Calculated Geometry	
Cu-Cl	2.199 Å
Cu-Cu	2.671 Å
Cu-Cl-Cu	74.8°
Cl-Cu-Cl	165.2°
Cu-Cu-Cu	60.0°

Computational Results: $(CuI)_n$ Geometries







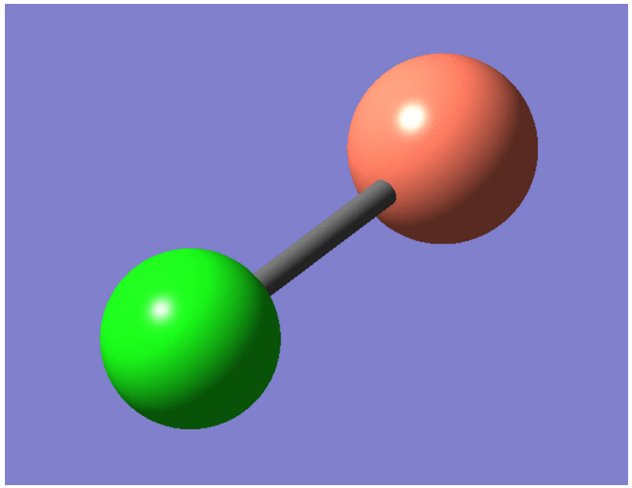
CuI Calculated Geometry	
Cu-I	2.393 Å

$(CuI)_2$ Calculated* Geometry	
Cu-I	2.565 Å
Cu-Cu	2.455 Å
Cu-I-Cu	57.2°
I-Cu-I	122.8°

$(CuI)_3$ Calculated* Geometry	
Cu-I	2.548 Å
Cu-Cu	2.252 Å
Cu-I-Cu	52.4°
I-Cu-I	63.8°
Cu-Cu-Cu	60.0°

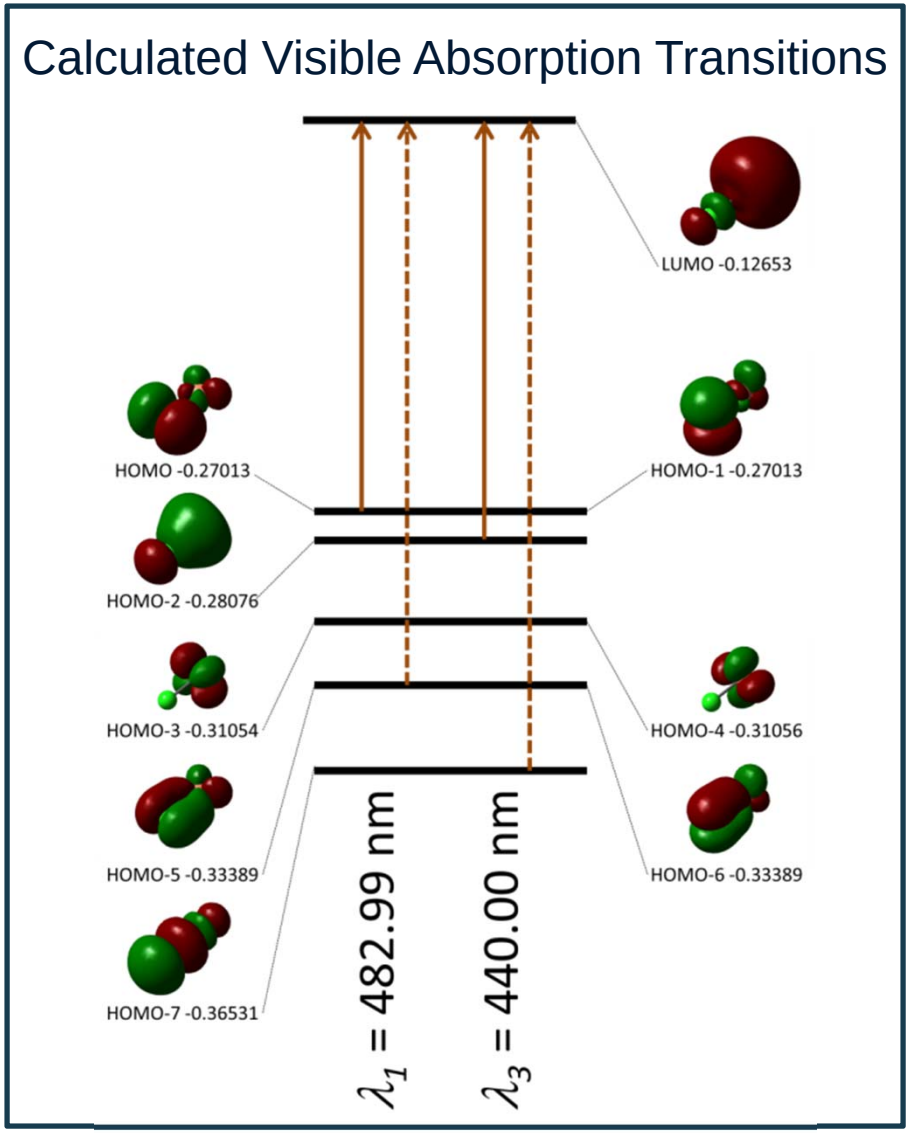
*Preliminary optimization using LANL2DZ

Computational Results: CuCl Monomer

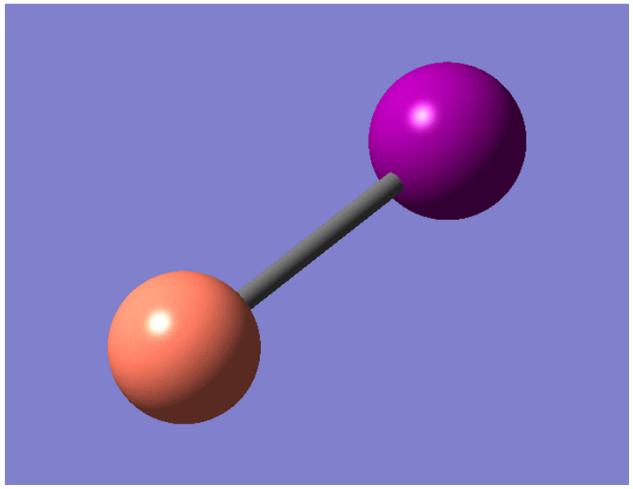


$\upsilon_{1(calc)}$ = 391.39 cm^{-1}

- Single vibration
- Two dominant visible electronic absorption bands

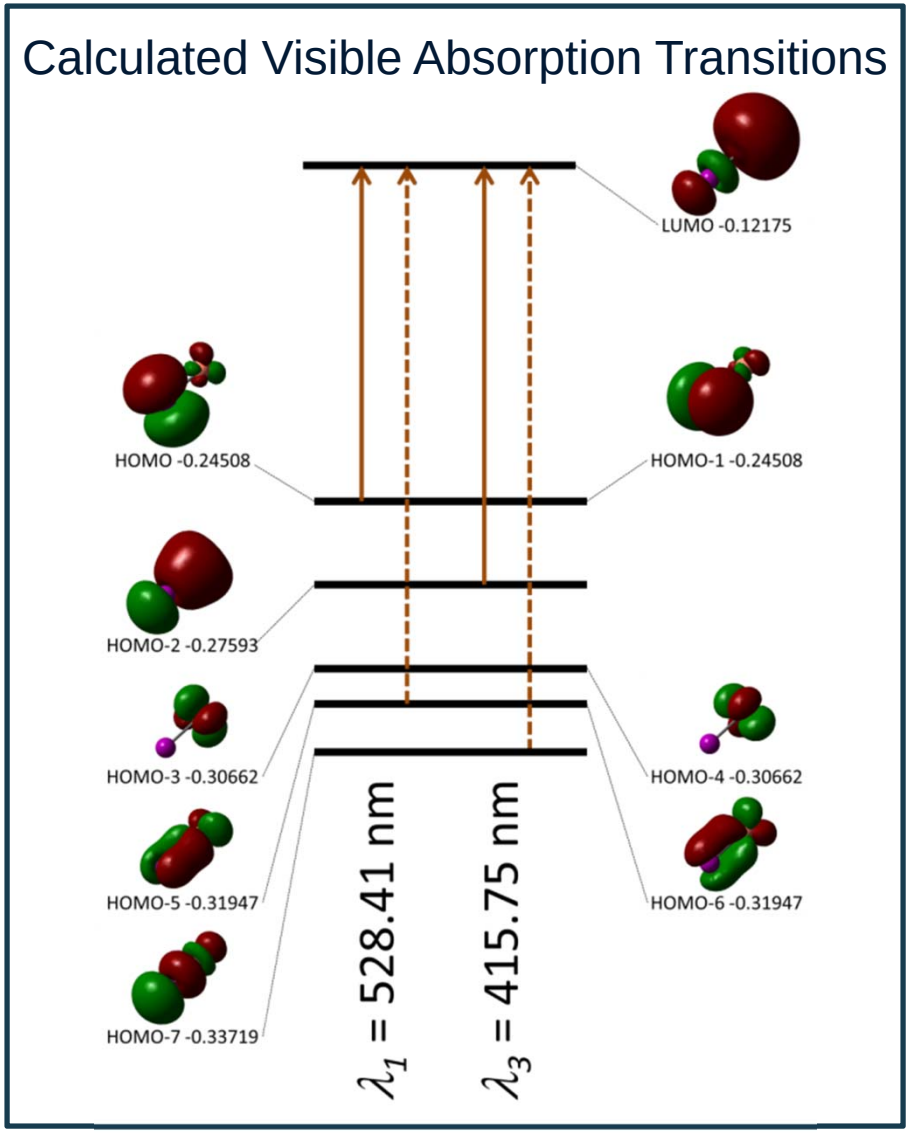


Computational Results: CuI Monomer



$\upsilon_{1(calc)}$ = 391.39 cm^{-1}

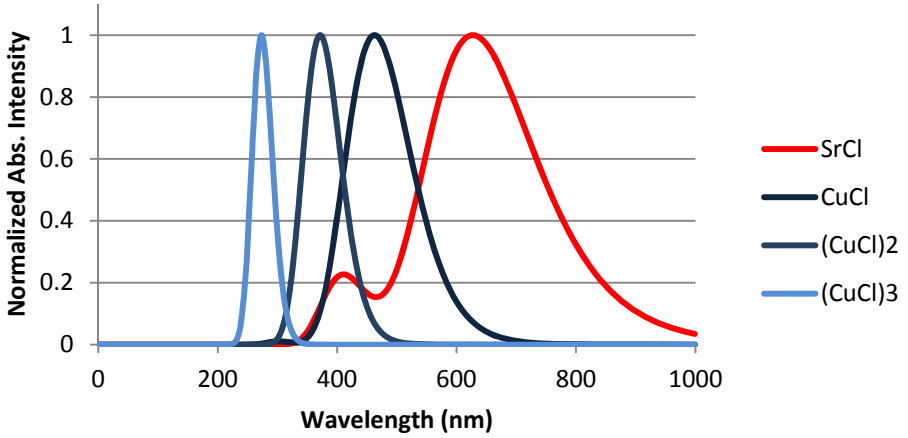
- Single vibration
- Two dominant visible electronic absorption bands
- Very similar to CuCl



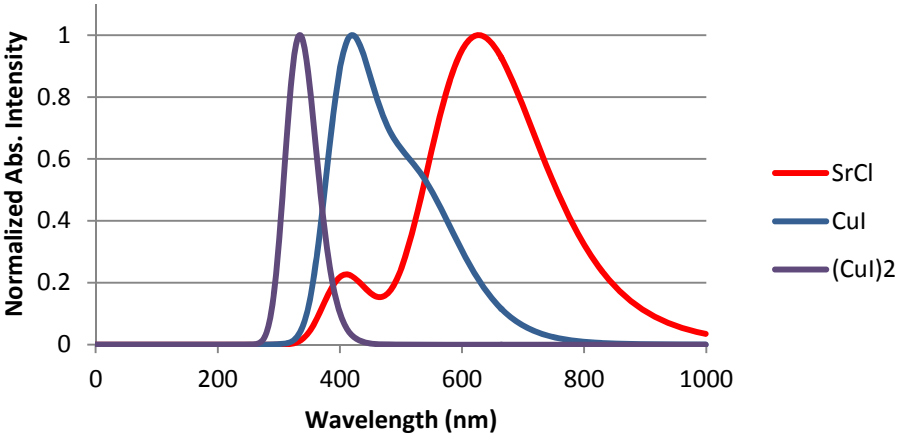
Preliminary Computational Results: Electronic Absorption

- SrCl calculated as reference
  - $\lambda_{1(calc)}$ = 647.28 nm
- Cluster growth produces hypsochromic absorption shift
- "Low" energy of first electronic transition for CuX monomers of interest

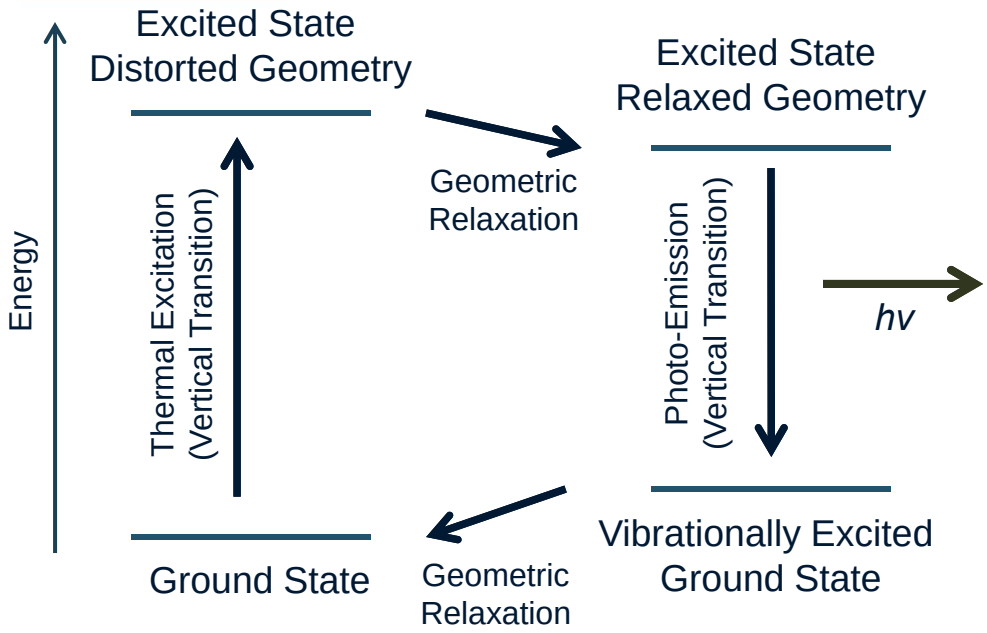
Calculated $(CuCl)_n$ Absorption Spectra



Calculated $(CuI)_n$ Absorption Spectra



Preliminary Computational Results: Emission Energies



Electronic Excitation vs. Emission Energies		
	Emission	Absorption
SrCl	648.4 nm	647.28 nm
CuCl	505.9 nm	482.99 nm
CuI	616.5 nm	528.41 nm

SrCl State Energies	
GS1	0 eV
ES1	1.9155eV
ES2	1.9138 eV
GS2	0.0017 eV
Emission	1.9121 eV
Emission	648.4 nm

CuCl State Energies	
GS1	0 eV
ES1	2.5670 eV
ES2	2.5278 eV
GS2	0.0762 eV
Emission	2.4506 eV
Emission	505.9 nm

CuI State Energies	
GS1	0 eV
ES1	2.3463 eV
ES2	2.2256 eV
GS2	0.2145 eV
Emission	2.0111 eV
Emission	616.5 nm

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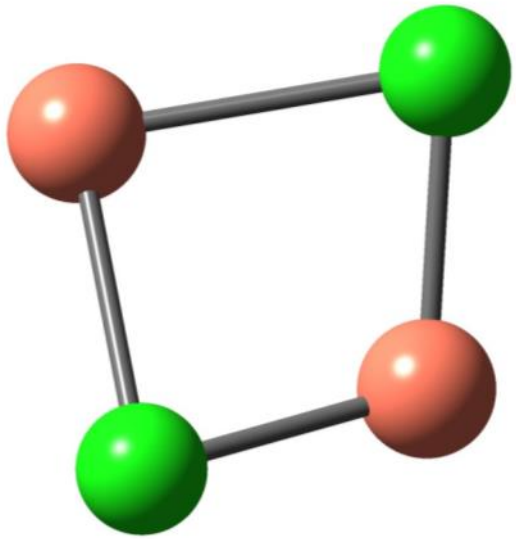
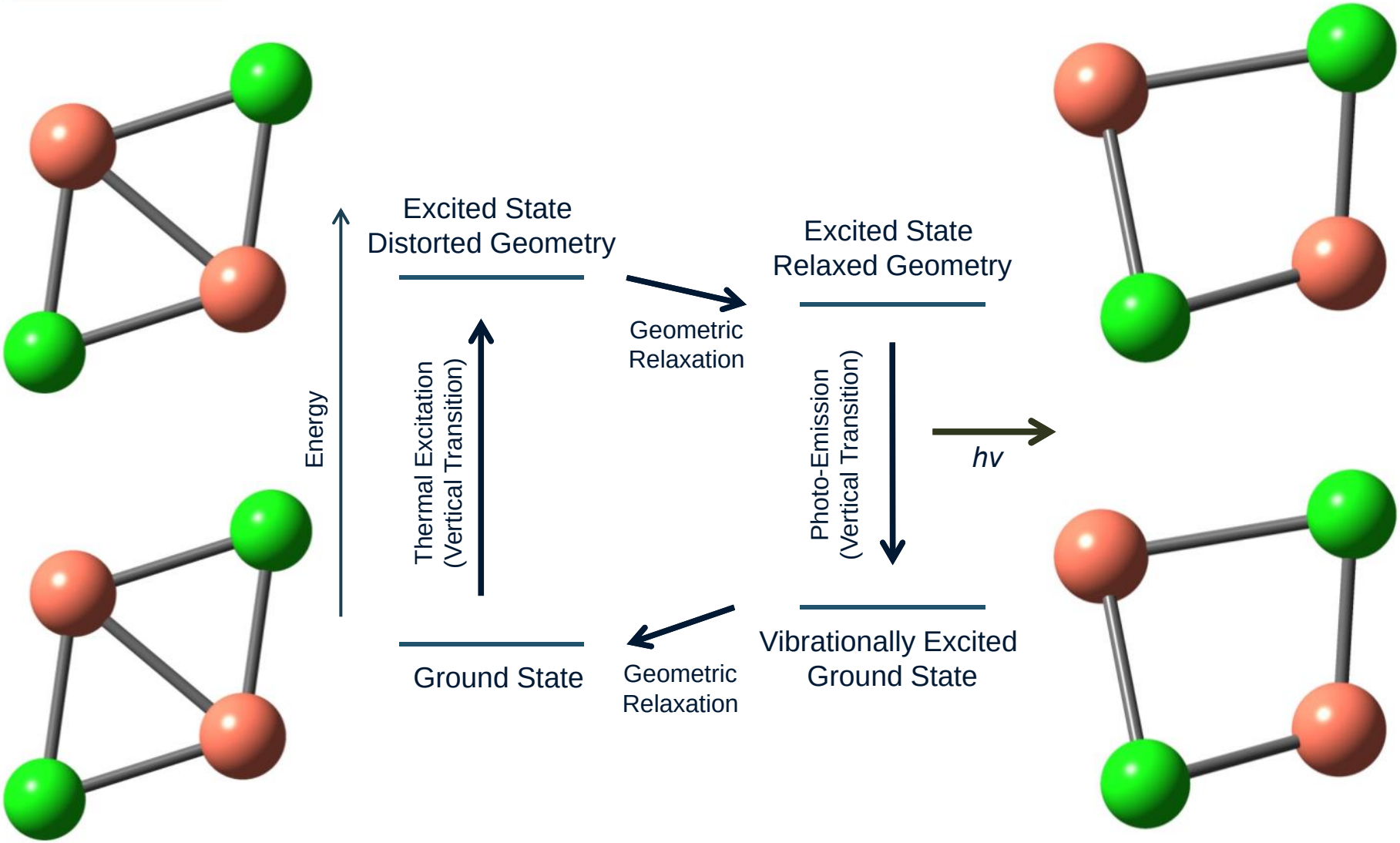
Preliminary Calc. Results: $(CuCl)_2$ Excited State Geometry

- Optimization of excited state geometries is ongoing
  - ES electronic structure causes distortion
  - Confirmation of minimized structures via vibrational calculations
  - This geometry is NOT minimized!
    - Software can sometimes produce misleading results if you aren't careful



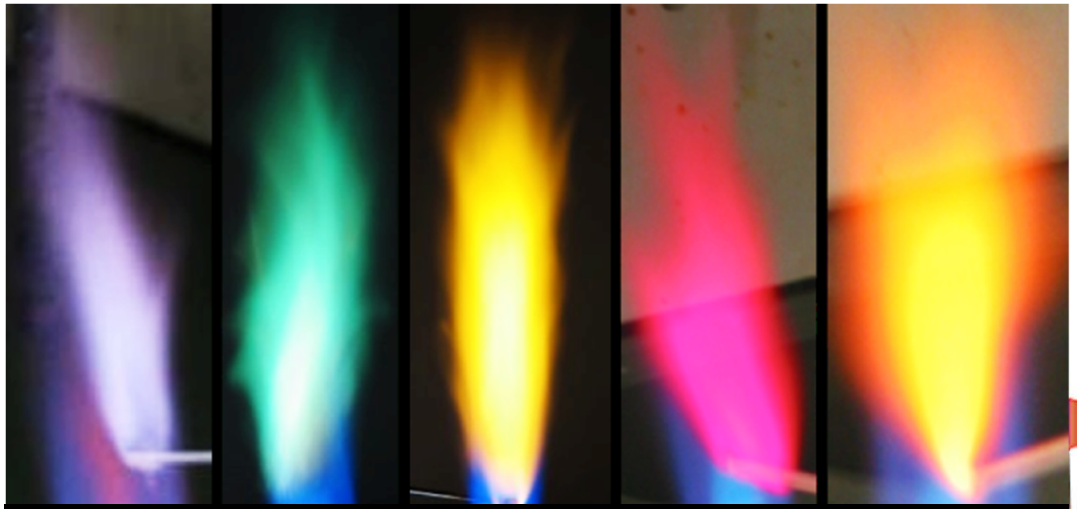
Calculated Geometry	
$Cu\text{-}Cl_1$	2.168 Å
$Cu\text{-}Cl_2$	2.558 Å
Cu-Cu	3.518 Å
Cu-Cl-Cu	77.3°
$Cl\text{-}Cu\text{-}Cl_1$	108.5°
$Cl\text{-}Cu\text{-}Cl_2$	86.9°

Computational Results: Trimeric Species



Spectroscopic Approach

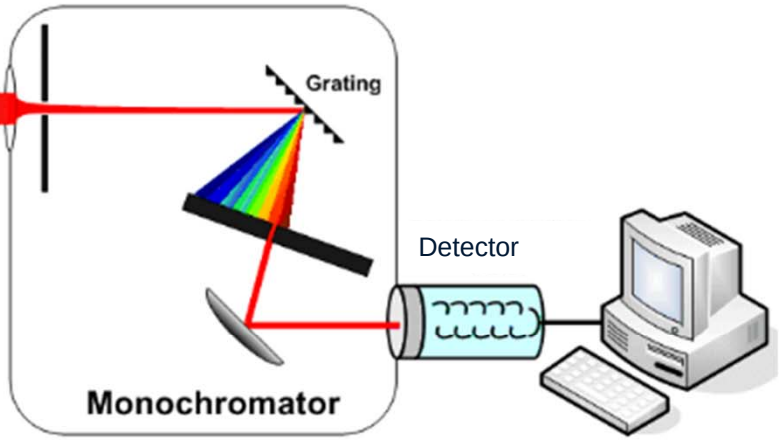
Flame Emission Spectroscopy



salts of arsenic, copper, sodium, lithium, and calcium burn within a flame

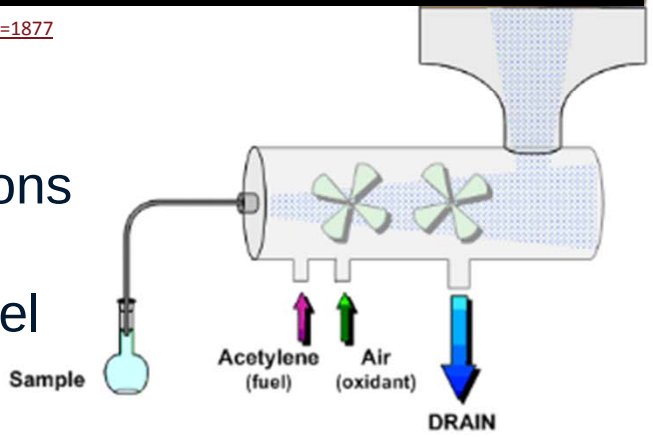
http://www.somethingaboutscience.com/?p=1877

- Metered gases to control flame temperature
- High-resolution spectroscopic measurements



http://faculty.sdmiramar.edu/fgarces/labmatters/instruments/aa/aa.htm

Concentrated metal salt solutions nebulized within premixed gas fuel



Conclusions

- Calculations of electronic emission spectra for $(CuX)_n$ species are underway
  - Preliminary calculations show all species have electronic excitation energies in correct range for possible blue emission
  - Vibrational contributions to emission spectra will be valuable for determining emitting species
- Future flame ionization studies will be used to for comparison with computational results

Acknowledgements

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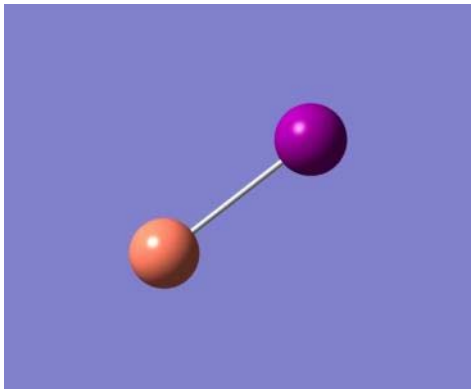
- Dr. Eric Miklaszewski, NSWC Crane
- Dr. Hank Webster, NSWC Crane
- Joshua Geary, NSWC Crane

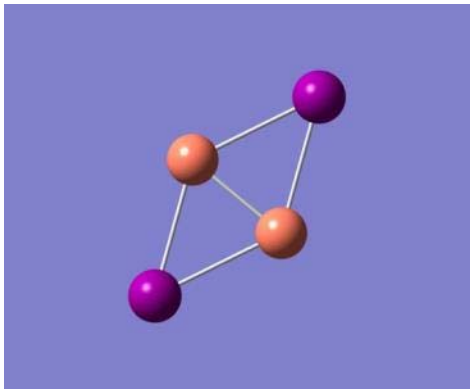
- Funding: NSWC Crane NISE/219 program

Backup Slides

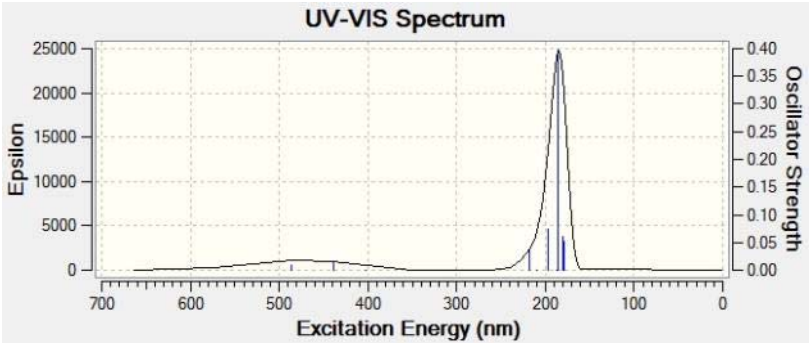
Preliminary Computational Results



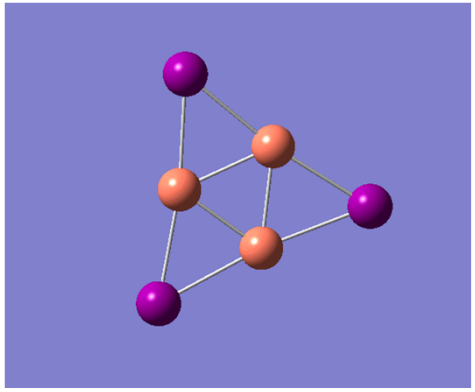
Copper Iodide Monomer (CuI)



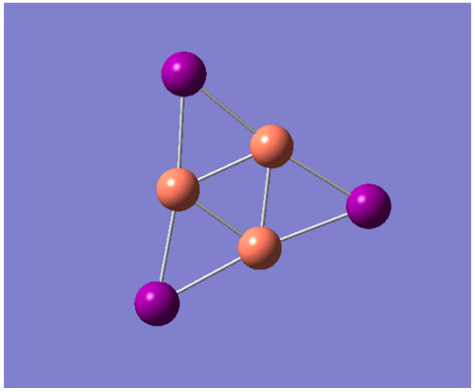
Copper Iodide Dimer (CuI)



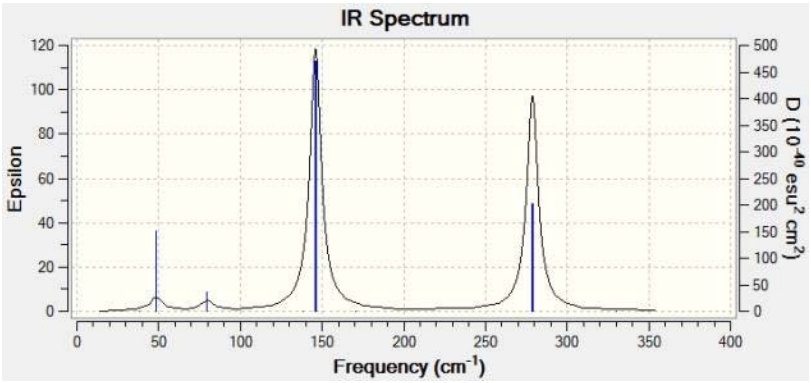
CuCl Calculated Electronic Absorption Spectrum



$(CuI)_3$– 146.2 cm^{-1} vibration



$(CuI)_3$ – 278.6 cm^{-1} vibration



$(CuI)_3$ Calculated Vibrational Spectrum